

# **THE DEVELOPMENT OF ANALYTICAL METHODS FOR PBMR TRISO SIC CHARACTERIZATION**

by

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# THE DEVELOPMENT OF ANALYTICAL METHODS FOR PBMR TRISO SIC CHARACTERIZATION

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## ABSTRACT

This experimental work aims to characterize the SiC layer of various Tri-Structural Isotropic (TRISO) coated fuel particles. In the first part of the work, Raman spectroscopy is used to qualitatively characterize the SiC TRISO layer and to identify the presence of silicon from peak positions. Free silicon poses a significant threat to the integrity of the SiC layer because it melts at 1414°C, significantly lower than the maximum operating temperature of 1550°C. Crystalline silicon is characterized with qualitative Raman spectroscopy by a 520 cm<sup>-1</sup> peak. Silicon is found to be preferentially concentrated along the SiC layer close to the inner pyrolytic carbon (IPyC) layer. Samples that were only mounted and polished are compared with those that have in addition also been etched. Disordering of the crystals and peak splitting necessitated the use of peak de-convolution. The 3C, 6H and 15R polytypes of SiC were identified.

The second part of the Raman spectroscopy work involves the development of calibration curves using peak areas from known binary mixtures (5%, 25%, 50% and 75% Si) to quantify the amount of silicon found relative to SiC. Initially the SiC polytypes used in these mixtures are 3C, 4H and 6H. Reasonably good logarithmic calibration fits were obtained with R<sup>2</sup> values of 0.996, 0.966 and 0.988 respectively. However some error accompanied the calibration values and an average of ten analyses yielded a more reliable

average. The calibration curve results made it possible to estimate the silicon content throughout the SiC layer for each sample, when combining the results of the qualitative and quantitative Raman spectroscopic study. Samples PO6 and PO8 revealed high peaks of crystalline silicon. When peak areas were quantified and related to the 3C calibration curve, as much as 60% silicon was calculated for both samples. Etching was found to slightly lower the silicon to SiC ratio. The calibration accuracy for the binary mixtures was checked by plotting calculated values against weighed-off values, yielding 3C, 4H and 6H straight-line fits with  $R^2$  values of 0.983, 0.941 and 0.981 respectively. These binary mixtures were analyzed with the SEM, which revealed variable particle size and segregation of silicon and SiC. Quantitative Raman spectroscopy is however known to be affected by a significant number of variables that are difficult to control. Attempts were made to decrease the scatter of the results from the calibration curve to yield more precise results. Two pure samples of silicon and SiC were studied separately, in attempts to better understand particle size and distortion effects. Distortion was found to have a greater impact on the scatter of peak area values than particle size. The scatter associated with pure sample peak areas casts doubt on the accuracy of the binary calibration curves.

Rietveld analysis using X-ray powder diffraction is used to further support the Raman spectroscopy work by qualitatively and quantitatively characterizing the phases involved in each TRISO particle, to a greater degree of accuracy than the Raman spectroscopy. Refinement components include 2H graphite, quartz, SiC (3C, 6H, 8H and 15R), silicon and tetragonal  $ZrO_2$ . Oxidized samples were compared with unoxidized samples. The outer pyrolytic carbon (OPyC) layer was oxidized (to improve the accuracy of quantitative measurements). Graphite percentages dominated the refinements with values ranging from 57% to 90% for unoxidized samples and 28% to 83% for oxidized samples. The 3C SiC polytype is the most abundant polytype and constitutes 78% to 83% of the SiC (unoxidized samples) and 82% to 90% (oxidized samples). Trace percentages of silicon were detected for PO6 (0.4%), PO8 (0.6%) and PO10 (0.1%) Quantitative XRD results are known to be accurate to around 1% at the  $3\sigma$  level. Calibration curves were also subsequently constructed from the same samples as those used for quantitative Raman spectroscopy by comparing the weighed-off values to the measured ones. The 3C,

4H and 6H  $R^2$ -fits are 0.991, 0.978 and 0.984 respectively. All the milled samples contained significant  $\alpha$ -Fe which contaminated the samples from the grinding process. After dissolving the  $\alpha$ -Fe in HCl a sample was tested to check the effect of the  $\alpha$ -Fe specifically on microabsorption. Microabsorption was found to be an insignificant effect.

The second part of the XRD work focused on the high-temperature stability of SiC up to 1400°C.  $Al_2O_3$  was used as the standard and the instrument was calibrated using its two independent lattice parameter values along the a-axis and c-axis to make temperature corrections. Temperature corrected curves (of SiC and graphite) were constructed, which superimposed the theoretical  $Al_2O_3$  curve along the a-axis and c-axis. The linear thermal expansion coefficients of SiC and graphite could then be determined from corrected lattice parameter values. The thermal expansion coefficients of G102 SiC had similar values to the literature values up to 800°C. Thereafter the experimental values had significantly higher thermal expansivity when compared to literature values. PO4 and PO9 thermal expansion coefficient values were higher below 500°C, but much closer as temperatures approached 1400°C. There was little correlation between G102, PO4 and PO9 graphite c-axis thermal expansion coefficient curves and literature values.

The third section of the work involves the characterization of the SiC layers of three of the samples by transmission electron microscopy using their selected area electron diffraction patterns. This facilitates the unequivocal characterization of the SiC polytypes. The 3C and 6H polytypes were identified. There is substantial disorder in the crystals. Planar defects of differing periodicity are seen along the [111] direction of the 3C polytype.

**Keywords:** SiC, silicon, characterization, Raman spectroscopy, X-ray powder diffraction, electron diffraction



## DECLARATION

I hereby declare that this thesis is my own work and that I have not incorporated the work forming its basis in any thesis submitted for another degree.

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Noko N Ngoepe

02 June 2009

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